

UK Patent Application GB 2 138 009 A

(43) Application published 17 Oct 1984

(21) Application No 8406429

(22) Date of filing 12 Mar 1984

(30) Priority data

(31) 58/038342 (32) 10 Mar 1983 (33) JP
58/189985 13 Oct 1983

(51) INT CL³
C08F 297/04

(52) Domestic classification
C3P FK
U18 1387 1384 3030 3042 3045 3069 C3P

(56) Documents cited
GB 1398431

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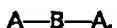
(58) Field of search
C3P

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(54) Block Copolymer of an Alkenyl Aromatic Compound and a Conjugated Diene

(57) A block copolymer of an alkenyl aromatic compound (e.g. styrene) and a conjugated diene (e.g. butadiene) has a combined alkenyl aromatic compound content of from 25 to 95% by weight and is represented by the formula:



Each block A is an alkenyl aromatic compound polymer block, the total of the two blocks A being from 50 to 97% by weight of the total combined alkenyl aromatic compound content of the copolymer. The central block B is a copolymer block of the conjugated diene and the alkenyl aromatic compound and is made up of from 2 to 10 taper blocks in which the amount of alkenyl aromatic compound gradually increases along the chain of each taper block; the weight ratio of alkenyl aromatic compound to conjugated diene in block B is from 3:97 to 85:15. In the copolymer, the total amount of chain segments made up of from 1 to 4 alkenyl aromatic compound monomer units is from 5 to 30% by weight of the total combined alkenyl aromatic compound content. Towards the lower end of the range of alkenyl aromatic compound contents, the copolymer is an elastomer having a good balance of tensile strength and elongation, whilst towards the upper end of this range, the copolymer is a resin, having a good balance of impact strength, tensile strength and elongation.

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FIG. I

NUMBER OF COMBINED STYRENE MONOMERS

2 MONOMERS

3 MONOMERS

4 MONOMERS

1 MONOMER

ABOUT 100 ST
MONOMERSCOMPARATIVE
EXAMPLE 6COMPARATIVE
EXAMPLE 5

EXAMPLE 1

 $n=1$ $n=2$ $n=3$ $n=4$ (ST CHAIN : $n = 1 \sim 100$)

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FIG. 2

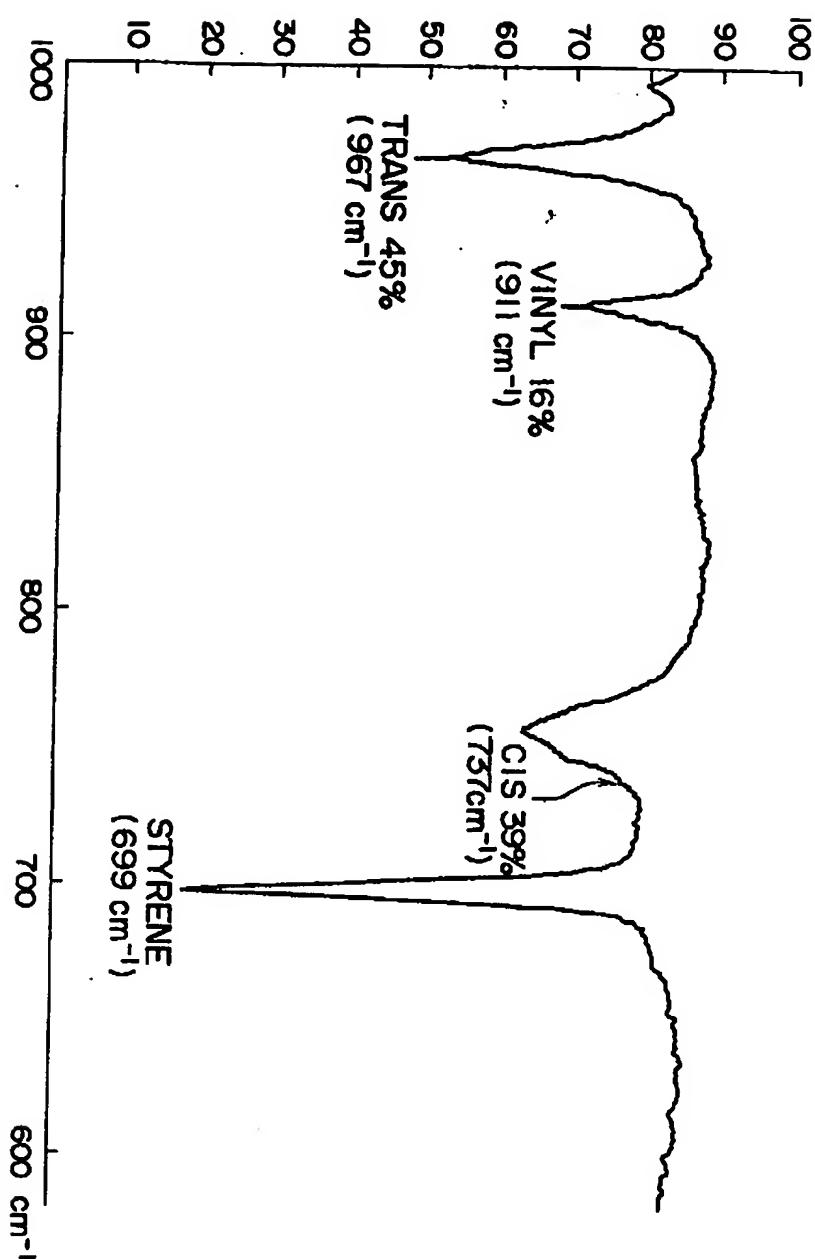
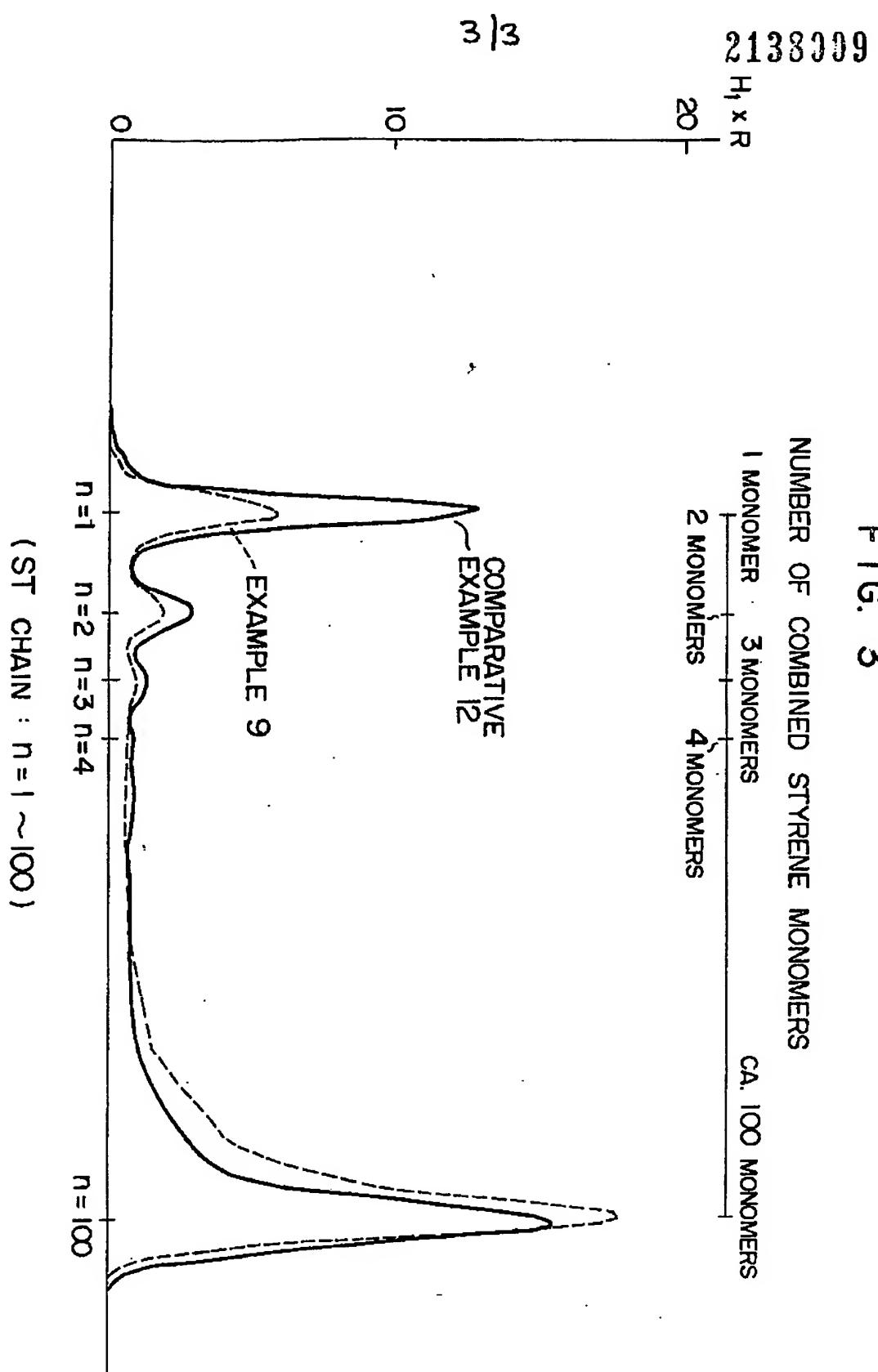


FIG. 3



SPECIFICATION**Block Copolymer of an Alkenyl Aromatic Compound and a Conjugated Diene, and a Process for Its Production**

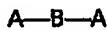
The present invention relates to a novel block copolymer of an alkenyl aromatic compound and a conjugated diene, which polymer can be an elastomer or a resin and which has an excellent balance of impact strength, tensile strength and elongation. 5

Recently, there has been a demand for a thermoplastic elastomer having a good balance of tensile strength and elongation and for a transparent, thermoplastic resin having a good balance of impact strength, tensile strength and elongation, produced by modifying polystyrene. Block copolymers 10 comprising a vinyl aromatic compound and a conjugated diene are well known and are disclosed in, for example, Japanese Patent Publications No. 28915/72, 3252/72, 2423/73 and 20038/73. However, the block copolymers obtained by these methods do not have a satisfactory balance of impact strength, tensile strength and elongation.

We have now discovered that such a balance can be achieved by preparing a specific block 15 structure.

Thus, in accordance with the present invention, there is provided a block copolymer of an alkenyl aromatic compound and a conjugated diene, in which:

- 1) the copolymer has a total combined alkenyl aromatic compound content of from 25 to 95% by weight (based on the total weight of the copolymer);
- 20 2) in the copolymer, the total weight of chain segments consisting of from 1 to 4 alkenyl aromatic compound units is from 5 to 30% by weight of the total alkenyl aromatic compound content; and
- 3) the copolymer is represented by the formula:



In which:

25 each block A is an alkenyl aromatic compound polymer block, the total weight of the two blocks A being from 50 to 97% by weight of the total combined alkenyl aromatic compound content; and 25

the block B represents a conjugated diene-alkenyl aromatic compound copolymer block in which the weight ratio of alkenyl aromatic compound units to conjugated diene units is from 3:97 to 85:15 and which comprises from 2 to 10 taper blocks, in which the amount of alkenyl aromatic compound units increases gradually along the chain of each taper block. 30

The block copolymer of the present invention contains the alkenyl aromatic compound in an amount of from 25 to 95% by weight, preferably from 28 to 90% by weight. If the amount of alkenyl aromatic compound is too small, the copolymer has a low tensile strength and hardness; on the other hand, if this amount is too large, the elongation and impact strength of the copolymer are inferior. 35 Within the lower part of this range of alkenyl aromatic compound contents, the block copolymer of the invention has the form of an elastomer; where this content is high, the block copolymer has the form of a resin.

Specifically, if it is desired to obtain the block copolymer in the form of an elastomer, the amount 40 of alkenyl aromatic compound is preferably from 25 to 55, more preferably from 28 to 50, percent by weight (based on the total weight of the copolymer). In this case, if the amount of alkenyl aromatic compound is below 25% by weight, the tensile strength is inadequate whereas, if this amount is too high, the elongation is inadequate. If it is desired to obtain the block copolymer in the form of a resin, the amount of alkenyl aromatic compound is preferably greater than 55% by weight but not more 45 than 95% by weight, more preferably from 60 to 90% by weight, the percentages being based on the total weight of the copolymer. If the amount of alkenyl aromatic compound is 55% by weight or less, the hardness of the resin is unsatisfactory, whereas, if this amount exceeds 95% by weight, the impact strength is inadequate.

The characteristic feature of the block copolymer of the present invention is that it may be 50 represented by the general formula A—B—A, in which the block B has an alkenyl aromatic compound content within a specific range and a number of taper blocks within a specific range, the block copolymer as a whole having a specified chain distribution of the alkenyl aromatic compound. These characteristic features allow the balance of the tensile strength and elongation to be improved remarkably and, when the block copolymer is in the form of a resin, the copolymer is transparent and has excellent impact strength. 55

The combined alkenyl aromatic compound content in block B of the block copolymer of the invention is from 3 to 85% by weight, more preferably from 5 to 60% by weight and most preferably from 5 to 55% by weight.

Where it is desired to obtain the block copolymer in the form of an elastomer, it is preferred that 60 the combined alkenyl aromatic compound content in the block B of the block copolymer should be from 3 to 15% by weight, more preferably from 5 to 10% by weight (the percentages being based on the total weight of the block B), and that the combined alkenyl aromatic compound content of the blocks A should be from 60 to 97% by weight, more preferably from 70 to 97% by weight of the total

combined alkenyl aromatic compound content in the entire copolymer. If the combined alkenyl aromatic compound content in the block B is less than 3% by weight, the copolymer has inferior tensile strength, whereas, if this content exceeds 15% by weight, the elongation is inadequate. Moreover, the block B comprises taper blocks, in which the combined alkenyl aromatic compound content increases gradually along the length of the chain of each taper block; the number of these taper blocks is from 2 to 10, preferably from 3 to 10 and more preferably from 3 to 7. If the number of taper blocks is less than 2, the elongation is inferior, whereas, if this number is greater than 10, tensile strength suffers. In the case of an elastomer, the chain distribution of alkenyl aromatic compound units is such that those chain segments consisting of from 1 to 4 alkenyl aromatic compound units make up from 5 to 30, preferably from 15 to 30, percent by weight of the total combined alkenyl aromatic compound content of the copolymer. The elongation of the copolymer is inferior if the amount of chain segments containing 4 or fewer monomer units is less than 5% by weight, whilst the tensile strength is inferior if this amount exceeds 30% by weight.

In order to obtain the block copolymer of the invention in the form of a resin, the combined alkenyl aromatic compound content in the block B is preferably from 3 to 85% by weight, more preferably from 10 to 55% by weight, and the combined alkenyl aromatic compound content in the blocks A is from 50 to 97, preferably from 70 to 97 and more preferably from 75 to 95, percent by weight of the total combined alkenyl aromatic compound content of the copolymer. If this combined alkenyl aromatic compound content of the block B of the copolymer is less than 3% by weight, the tensile strength is inadequate, whereas the elongation is unsatisfactory if this content exceeds 85% by weight. In the block B, the number of taper blocks is from 2 to 10, preferably from 3 to 10. If this number is less than 2, the elongation is inferior, whilst impact strength and tensile strength are inferior, if the number exceeds 10.

Where the block copolymer is in the form of a resin, the chain distribution of alkenyl aromatic compound monomer units in the block copolymer is preferably such that the amount of chain segments containing from 1 to 4 alkenyl aromatic compound units is from 5 to 25, more preferably from 10 to 20, percent by weight of the total combined alkenyl aromatic compound content. If this amount is less than 5% by weight, the elongation is insufficient, whereas, if it exceeds 25% by weight, the copolymer has inadequate impact strength.

The invention also provides a process for preparing a block copolymer of an alkenyl aromatic compound and a conjugated diene, said copolymer having a combined alkenyl aromatic content of from 25 to 95% by weight and being represented by the formula



(in which A and B are as defined above), which process comprises:

(a) adding to an organolithium initiator in a hydrocarbon solvent (and preferably including an ether or a tertiary amine) an alkenyl aromatic compound in an amount of from 8 to 45% (preferably from 10 to 40%) by weight of the total amount of monomers used in the process, and substantially completely polymerising the same;

(b) thereafter, adding, in from 2 to 10 (preferably from 3 to 10 and more preferably from 3 to 7) portions, a mixture of from 15 to 97% by weight of a conjugated diene and from 3 to 85% by weight of the same alkenyl aromatic compound as in step (a), these percentages being based on the weight of the mixture in step (b), and substantially completely polymerising the mixture after addition of each portion; and

(c) thereafter, adding the same alkenyl aromatic compound as in step (a) in an amount of from 8 to 45% (preferably from 10 to 40%) by weight of the total amount of monomers used in the process and polymerising the same.

Specifically, in order to produce the block copolymer in the form of an elastomer, in which the copolymer is as defined above but has a combined alkenyl aromatic compound content of from 25 to 55% by weight, the process preferably comprises the steps:

(a) adding to an organolithium initiator in a hydrocarbon solvent an alkenyl aromatic compound in an amount of from 8 to 40% (preferably from 10 to 25% by weight of the total amount of monomers used in the process, and substantially completely polymerising the same;

(b) thereafter, adding, in from 2 to 10 (preferably from 3 to 10) portions, a mixture of from 85 to 97% by weight of a conjugated diene and from 3 to 15% by weight of the same alkenyl aromatic compound as in step (a), these percentages being based on the weight of the mixture in step (b), and substantially completely polymerising the mixture after addition of each portion; and

(c) thereafter, adding the same alkenyl aromatic compound as in step (a) in an amount of from 8 to 40% (preferably from 10 to 25%) by weight of the total amount of monomers used in the process and polymerising the same.

In order to produce the block copolymer in the form of a resin, in which the copolymer is as defined above but has a combined alkenyl aromatic compound content which is greater than 55% by weight but not more than 95% by weight, the process comprises:

- (a) adding to an organolithium initiator in a hydrocarbon solvent an alkenyl aromatic compound in an amount of from 20 to 45% (preferably from 25 to 40%) by weight of the total amount of monomers used in the process, and substantially completely polymerising the same;
- 5 (b) thereafter, adding, in from 2 to 10 (preferably from 3 to 10) portions, a mixture of from 15 to 97% by weight of a conjugated diene and from 3 to 85% by weight of the same alkenyl aromatic compound as in step (a), these percentages being based on the weight of the mixture in step (b), and substantially completely polymerising the mixture after addition of each portion; and
- 10 (c) thereafter, adding the same alkenyl aromatic compound as in step (a) in an amount of from 20 to 45% (preferably from 25 to 40%) by weight of the total amount of monomers used in the process and polymerising the same.
- In step (b) of each of the above processes, a mixture of the two monomers is added in from 2 to 10 portions. It is preferred that the amount of monomer added in each portion should be the same and it is desirable that 100% of the monomer should be polymerised after each addition and before the next addition. A mixture of the two monomers may be added as such to the reaction system; alternatively, the two monomers may be added separately but simultaneously.
- If desired, a conjugated diene [preferably the same as in step (b)] may be added and polymerised between steps (b) and (c); it forms part of the block B.
- A copolymer having the desired chain distribution of the alkenyl aromatic compound can be obtained by carrying out these polymerisation processes in a hydrocarbon solvent having added thereto an ether or a tertiary amine. When an ether or tertiary amine is present, the amount of chain segments containing from 1 to 4 alkenyl aromatic compound monomer units is increased. The amount of these chains is preferably from 5 to 30%, more preferably from 10 to 30%, by weight of the total amount of alkenyl aromatic compound. If the amount of these chain segments is less than 5% by weight, the elongation of the copolymer is unsatisfactory, whereas, if this amount exceeds 30% by weight, the tensile strength and impact strength are inadequate.
- In order to achieve suitable control of the chain distribution of the alkenyl aromatic compound, the amount of ether or tertiary amine used is preferably from 0.005 to 5 parts, more preferably from 0.005 to 0.5 part, by weight per 100 parts by weight of monomers. Suitable ethers and tertiary amines include tetrahydrofuran, diethyl ether, anisole, dimethoxybenzene, ethylene glycol dimethyl ether, triethylamine, N,N-dimethylaniline and pyridine.
- Examples of suitable alkenyl aromatic compounds which may be used in the present invention include styrene, alpha-methylstyrene, *p*-methylstyrene, *m*-methylstyrene, *o*-methylstyrene, *p*-*t*-butylstyrene, dimethylstyrene and vinylnaphthalene, of which styrene is preferred. A single one of these alkenyl aromatic compounds is preferably used, but, if desired, a mixture of two or more alkenyl aromatic compounds may be used. The blocks A should consist essentially or completely of units derived from the alkenyl aromatic compound(s). Preferably, the blocks A consist solely of the alkenyl aromatic compound(s), but, if desired, they may contain a minor proportion (such as to leave substantially unaffected their essential characteristics) of another copolymerisable monomer, as is well known in the art.
- Suitable conjugated dienes include butadiene, isoprene and piperylene, of which butadiene is preferred. A single one of these conjugated dienes is preferably used; however, if desired, a mixture of two or more may be employed.
- The weight average molecular weight of the block copolymer of the present invention is preferably from 10,000 to 800,000, more preferably from 50,000 to 500,000. Within this range, the weight average molecular weight of the blocks A is preferably from 3,000 to 150,000 and the weight average molecular weight of the block B is preferably from 5,000 to 340,000. Particularly when the block copolymer is in the form of an elastomer, the weight average molecular weight of the blocks A is preferably from 3,000 to 80,000 and the weight average molecular weight of the block B is preferably from 44,000 to 340,000. When the block copolymer is in the form of a resin, the weight average molecular weight of the block B is preferably from 5,000 to 200,000, and that of the blocks A is preferably from 3,000 to 150,000.
- The block copolymer of the present invention can be prepared either by an isothermal polymerisation process or by an adiabatic polymerisation process. The polymerisation temperature is preferably within the range from 30°C to 120°C.
- Examples of hydrocarbon solvents which may be used in the processes of the invention include cyclopentane, cyclohexane, benzene, ethylbenzene or xylene, or mixtures of one of these solvents with pentane, hexane, heptane, butane or the like.
- Examples of organolithium compounds which may be used as the initiator in the process of the invention include butyllithium, sec-butyllithium, t-butyllithium, hexyllithium, Isohexyllithium, phenyllithium or naphthyllithium, and the amount of organolithium compound used is preferably from 0.04 to 1.0 part by weight per 100 parts by weight of the monomers.
- The block copolymer of the present invention can be used alone or, if desired, in admixture with another plastics material, for example: polystyrene; a styrene copolymer, such as styrene-methyl methacrylate copolymer or styrene-acrylonitrile copolymer; a graft copolymer, such an ABS resin; a

- polyolefin, such as polyethylene or polypropylene; polyvinyl chloride; polyvinyl acetate; a polyester; a polyether; a polyacetal; or a polycarbonate; or it may be used in admixture with a rubber, such as 1,2-polybutadiene, BR, SBR, NBR or EPR. These mixtures can be used for various purposes, for example: injection-moulded articles, such as food containers or footwear; flow-moulded articles, such as toys or articles for daily use; or compression-moulded articles, such as automobile parts; parts of electrical devices, packaging, sheets or plates.
- Furthermore, because the block copolymers of the invention are soluble in hydrocarbon solvents, they may also be used effectively as adhesives. In addition, they can be used for altering the physical properties of other rubbers (such as SBR or NBR) or of plastics (such as polystyrene). For example, they can be used with rubbers to produce crepe sponges or with plastics materials to improve the impact resistance and other properties of polystyrene for general use. The block copolymers can also be foamed for various uses.
- The invention is further illustrated by the following Examples, Comparative Examples and accompanying drawings. In the accompanying drawings:
- Figure 1 shows the styrene chain distribution curves obtained by gel-permeation chromatography of the copolymers produced as described in Example 1 and in Comparative Examples 5 and 6, said curves having been obtained by the method of oxidative degradation with ozone;
- Figure 2 shows the infrared absorption spectrum of the copolymer obtained as described in Example 9; and
- Figure 3 shows the chain distribution curve of the copolymers obtained as described in Example 9 and Comparative Example 12.
- The various measurements described in the Examples were carried out by the following methods:
- Where the block copolymers are in the form of elastomers (Examples 1—8 and Comparative Examples 1—9), tensile strength (T_b) and elongation (E_b) were measured by the method of Japanese Industrial Standard (JIS) K-6301.
- Where the block copolymers are in the form of a resin (Examples 9—12 and Comparative Examples 10—14), impact strength, tensile strength and elongation were measured by the method of JIS K-6871.
- The transparency test was based upon ASTM D-1003.
- The styrene chains were measured by the method developed by Professor Tanaka et al., the Tokyo University of Agriculture and Technology (Abstracts of The Polymer Society, Japan, Vol. 29, No. 7, page 2055).
- Hardness was measured on the R scale according to ASTM D-785.
- The total amount of styrene was measured in infrared spectroscopy.
- EXAMPLE 1**
- Into a washed and dried autoclave provided with a stirrer and a jacket were charged, under a nitrogen atmosphere, 4,500 g of cyclohexane and 1 g of tetrahydrofuran, after which the internal temperature of the autoclave was raised to 70°C. Subsequently, a hexane solution containing 0.5 g of butyllithium, followed by 130 g of styrene, were added to the mixture thus obtained and polymerised at 70°C for 60 minutes. The conversion of styrene was 100%.
- A mixture of 15 g of styrene and 115 g of butadiene was then added and polymerisation was again carried out at 70°C for 60 minutes. The conversions of styrene and butadiene were 100%. Addition of an identical mixture and polymerisation were repeated a further two times. Subsequently, 115 g of butadiene were added and polymerisation was carried out at 70°C until the conversion reached 100%.
- A further 130 g of styrene were added and polymerisation was carried out for 60 minutes. The conversion was 100%.
- The temperature during polymerisation was controlled so that it always kept at 70°C. After completion of the polymerisation, 2,6-di-t-butyl-p-cresol was added to the polymer solution, after which the cyclohexane was removed by heating, giving the desired copolymer.
- Examples 2—8 and Comparative Examples 1—10**
- Polymerisation was carried out using the same recipes and conditions as in Example 1, except that the amounts of styrene, butadiene and tetrahydrofuran were varied, as shown in Table 1, which also gives the same details for Example 1. The results obtained in all these Examples and Comparative Examples are shown in Table 2.

TABLE 1

	Styrene (g)			Amount of Butadiene (g)	Amount of Tetra- hydrofuran (g)	Number of Additions of Monomer in the B Portion
	Initial Styrene Content in A Portion	Styrene Content in B Portion	Post-added Styrene Content in A Portion			
Example 1	130	45	130	460	1	4
	2	145	145	460	1	4
	3	123	123	460	1	4
	4	130	130	462	1	7
	5	95	95	536	1	4
	6	175	175	380	1	4
	7	130*	130*	460	1	4
Comparative Example 1	65	24	65	612	1	4
	2	208	208	305	1	4
	3	300	300	460	1	4
	4	96	96	460	1	4
	5	130	130	460	0	4
	6	130	130	460	50	4
	7	130	130	460	1	2
	8	130	130	460	1	20

Note:

*p-Methylstyrene was used in place of styrene.

TABLE 2

	Proportion of Styrene Chains of n being 1 to 4 (%)	Combined Styrene Content in B Portion (%)	Total Combined Styrene Content (%)	Molecular Weight of A Portion ($\times 10^4$)	Molecular Weight of B Portion ($\times 10^4$)	Tensile Strength (kg/cm ²)	Elongation (%)
Example 1	22	9	40	1.8	7.2	180	1,000
	26	3	40	2.1	6.8	243	950
	19	12	40	1.7	7.4	165	1,050
	27	9	40	1.8	7.3	174	1,100
	21	8	30	1.4	8.3	156	1,200
	23	7	50	2.5	5.9	320	850
	22	9	40	1.8	7.2	182	1,000
Comparative Example 1	24	4	20	0.9	9.1	127	1,100
	25	13	60	2.9	4.9	335	700
	21	1	40	4.3	8.7	273	750
	24	20	40	1.4	8.2	138	800
	0	9	40	1.8	9.1	135	1,100
	67	9	40	1.8	9.1	125	1,000
	19	9	40	1.8	9.1	175	800
	23	9	40	1.8	9.1	146	950

The important variations in these Examples and Comparative Examples are as follows:

EXAMPLES 2 and 3

5 The combined styrene contents in the block B were 3% and 12%, respectively.

5

EXAMPLE 4

The monomer to form the block B was added in 7 portions, of which 6 consisted of mixtures of styrene and butadiene and the last was butadiene alone.

EXAMPLES 5 and 6

10 The total combined styrene contents were 30% and 50%, respectively.

10

EXAMPLE 7

p-Methylstyrene was used in place of styrene.

Comparative Examples 1 and 2

The total combined styrene contents were 20% and 60%, respectively.

15 Comparative Examples 3 and 4

The combined styrene content in the block B was 1% or 20%, respectively. (Although Comparative Examples 2 and 4 provide block copolymers falling within the present invention, they are comparative in the sense that the present series of Examples and Comparative Examples illustrates the preparation of elastomers.)

15

Comparative Examples 5 and 6

No tetrahydrofuran or a great excess of tetrahydrofuran (6.5 g per 100 g of monomer), respectively, were added.

Comparative Examples 7 and 8

- 5 The monomer to make up block B was added in 2 or 20 portions, respectively. In each case, the last portion added consisted of butadiene alone and the earlier portion or portions consisted of the specified mixture of styrene and butadiene. 5

The block copolymers produced as described in Examples 1—7 had a much better balance of tensile strength and elongation than those produced as described in Comparative Examples 1—8.

- 10 Figure 1 shows the distribution curves of styrene chains by the oxidative degradation method, using ozone, following the procedure developed by Tanaka et al., for the copolymers of Example 1 and Comparative Examples 5 and 6. The results shown in Table 3 are obtained from the data of Figure 1. The symbol "n" is the number of repeating monomer units in the chain segment. 10

TABLE 3

	Length of Styrene Chain Segment				
	n=1	n=2	n=3	n=4	n 5
Example 1	14%	4	3	1	78
Comparative Example 5	0	0	0	0	100
Comparative Example 6	48	10	7	4	33

Example 8 and Comparative Example 9

- A mixture of 12% by weight of the block copolymer obtained as described in Example 1 and 88% by weight of a polystyrene (Toporex-525, a trade name of Mitsui Toatsu) was prepared, and a sheet of thickness 0.2 mm was formed from the mixture at a moulding temperature of 180°C. A similar sheet 20 was prepared from the polystyrene alone (Comparative Example 9). The physical properties of the sheets were examined and the results are shown in Table 4. 20

TABLE 4

		Impact resistance of sheet (Kg-cm/mm)	Tensile Strength (Kg/cm ²)	Elongation (%)	Haze (%)
Example 8	Polystyrene/the block copolymer (88/12, weight ratio)	20	320	21	31
Comparative Example 9	Polystyrene	11	70	3	2

EXAMPLE 9

5 Into a washed and dried autoclave provided with a stirrer and a jacket were charged, under a nitrogen atmosphere, 5,000 g of cyclohexane and 1 g of tetrahydrofuran, after which the internal temperature of the autoclave was raised to 70°C. A hexane solution containing 0.64 g of butyllithium, followed by 300 g of styrene, was added to the resulting mixture, which was then polymerised at 70°C for 60 minutes. The conversion of styrene was 100%.

10 A mixture of 50 g of styrene and 125 g of butadiene was then added and polymerization was carried out at 70°C for 80 minutes. The conversions of styrene and butadiene were 100%. Addition of an identical mixture and polymerisation were repeated further 2 times. 125 g of butadiene were then added and polymerisation was carried out at 70°C until the conversion reached 100%.

15 A further 300 g of styrene were then added and polymerisation was carried out at 70°C for 60 minutes. The conversion was 100%.

The temperature was controlled during the polymerisation, so that it always kept at 70°C. After completion of the polymerisation, 2,6-di-t-butyl-p-cresol was added to the polymer solution, and then 15 the cyclohexane was removed by heating, to give the block copolymer.

Examples 10—12 and Comparative Examples 10—14

Polymerisation was carried out with the same recipe and under the same conditions as in Example 9, except that the amounts of styrene, butadiene and tetrahydrofuran were varied as shown in Table 5 and that the addition and polymerisation of butadiene alone were omitted. Table 5 also summarises the details of Example 9.

20 Table 6 shows the molecular characteristics of the block copolymers obtained as described in Examples 9—12 and Comparative Examples 10—14, and Table 7 shows the results of evaluation of the physical properties of these block copolymers.

TABLE 5
Polymerization Formulation

25

20

25

	Styrene (g)			Amount of Butadiene (g)	Amount of Tetrahydrofuran (g)	Number of Additions of Monomer in B Portion
	Initial Styrene Content In A Portion	Styrene Content in B Portion	Post-Added Styrene Content in A Portion			
Example 9	300	150	300	500	1	4
10	450	225	450	125	1	6
11	375*	188*	375*	313	1	2
12	375**	188**	375**	313	1	2
Comparative Example 10	225	50	225	750	1	3
11	375	475	375	25	1	3
12	325	250	325	350	75	3
13	425	200	425	200	1	12
14	400	200	400	250	1	1

Note:

*p-Methylstyrene was used in place of the styrene.

** α -Methylstyrene was used in place of the styrene.

TABLE 6
Molecular Properties

	Total Combined Styrene Content (%)	Combined Styrene Content in B Portion (%)	Proportion of Styrene Chain of n being 1-4 (%)	Molecular Weight of A Portion ($\times 10^4$)	Molecular Weight of B Portion ($\times 10^4$)
Example 9	60	23	13	3.3	7.2
	10	64	15	5.0	3.9
	11	75	17	4.2	5.6
	12	75	18	4.2	5.6
Comparative Example 10	40	6	7	2.5	8.9
	11	98	21	4.2	5.6
	12	72	28	3.8	6.7
	13	84	14	4.7	4.4
	14	80	16	4.4	5.0

TABLE 7
Evaluation Results of Physical Properties

	Tensile Strength (kg/cm ²)	Elongation at Break (%)	Izod Impact Strength (Notched) (kg-cm/cm)	Rockwell Hardness (R Scale)	Total Light Transmission (%)	Haze (%)
Example 9	270	530	7.5	35	89	4
	10	430	21	114	91	3
	11	350	54	88	88	4
	12	340	58	87	89	4
Comparative Example 10	180	800	Immeasurable	too low to measure	87	4
	11	400	5	119	89	4
	12	290	43	83	91	4
	13	300	34	97	88	3
	14	330	14	94	89	4

The important features of the Examples and Comparative Examples are as follows:

EXAMPLE 9

The total combined styrene content was 60%, the combined styrene content of the block B was 23% and the monomer to form the block B was added in 4 portions, of which the last was butadiene alone.

EXAMPLE 10

The total combined styrene content was 90%, the combined styrene content of the block B was

64% and the monomer to form the block B was added in 6 portions, all being mixtures of styrene and butadiene.

EXAMPLE 11

p-Methylstyrene was used in place of styrene, the total combined *p*-methylstyrene content was 5 75%, the combined *p*-methylstyrene content of the block B was 37%, and the monomer to form the block B was added in two portions (both composed of a mixture of *p*-methylstyrene and butadiene). 5

EXAMPLE 12

Alpha-methylstyrene was used in place of styrene, the total combined alpha-methylstyrene content was 10 75%, the combined alpha-methylstyrene content of the block B was 37%, and the monomer to form the block B was added in 2 portions (both composed of a mixture of alphamethyl- 10 styrene and butadiene).

Comparative Example 10

The total combined styrene content was 40% (although this falls within the invention, this Example is comparative in the sense that the aim of this set of Examples and Comparative Examples is 15 to produce a resin). 15

Comparative Example 11

The total combined styrene content was 98%.

Comparative Example 12

An excess of tetrahydrofuran (6.0 g per 100 g of monomer) was used.

20 Comparative Example 13

The monomer to form the block B was added in 12 portions, all of which were mixtures of styrene and butadiene. 20

Comparative Example 14

The monomer mixture to form the block B was added in a single portion.

25 As can be seen from Table 7, the block copolymers of Examples 9—12 have a much better 25 balance of impact strength, tensile strength and elongation at break than those of Comparative Examples 10—14.

CLAIMS

30 1. A block copolymer of an alkenyl aromatic compound and a conjugated diene, in which:
1) the copolymer has a total combined alkenyl aromatic compound content of from 25 to 95% by 30 weight (based on the total weight of the copolymer);
2) in the copolymer, the total weight of chain segments consisting of from 1 to 4 alkenyl aromatic compound units is from 5 to 30% by weight of the total alkenyl aromatic compound content; and
3) the copolymer is represented by the formula:



35 In which:
each block A is an alkenyl aromatic compound polymer block, the total weight of two blocks A being from 50 to 97% by weight of the total combined alkenyl aromatic compound content; and
40 the block B represents a conjugated diene-alkenyl aromatic compound copolymer block in which the weight ratio of alkenyl aromatic compound units to conjugated diene units is from 3:97 to 85:15 and which comprises from 2 to 10 taper blocks in which the amount of alkenyl aromatic compound units increases gradually along the chain of each taper block.
45 2. A copolymer according to claim 1, in which the weight ratio of alkenyl aromatic compound to conjugated diene in block B is from 5:95 to 80:40.
3. A copolymer according to claim 1, in which the total of the two blocks A is from 70 to 97% by weight of the total combined alkenyl aromatic compound content in the copolymer.
4. A copolymer according to any one of the preceding claims in which the block B has from 3 to 10 of said taper blocks.
50 5. A copolymer according to any one of the preceding claims, in the form of an elastomer, in which the total combined alkenyl aromatic compound content of the copolymer is from 25 to 55% by weight, and the weight ratio of alkenyl aromatic compound to conjugated diene in the block B is from 3:97 to 15:85.
55 6. A copolymer according to claim 5, in which the number of said chain segments consisting of from 1 to 4 alkenyl aromatic compound units is from 15 to 30% by weight of the total alkenyl aromatic compound content. 55

7. A copolymer according to any one of claims 1 to 4, in the form of a resin, in which the total combined alkenyl aromatic compound content of the copolymer is greater than 55% by weight but not more than 95% by weight.
8. A copolymer according to claim 7, having a combined alkenyl aromatic compound of from 60 to 90% by weight of the copolymer.
- 5 9. A copolymer according to claim 7 or claim 8, in which the total weight of said chain segments consisting of from 1 to 4 alkenyl aromatic compound units is from 5 to 25% by weight of the total alkenyl aromatic compound content.
- 10 10. A copolymer according to any one of the preceding claims, having a weight average molecular weight of from 10,000 to 800,000.
- 10 11. A copolymer according to claim 10, in which said weight average molecular weight is from 50,000 to 500,000.
- 15 12. A copolymer according to claim 11, in which the weight average molecular weight of each block A is from 3,000 to 150,000 and the weight average molecular weight of the block B is from 5,000 to 340,000.
- 15 13. A copolymer according to any one of the preceding claims, in which the alkenyl aromatic compound is styrene, alpha-methylstyrene, *p*-methylstyrene, *m*-methylstyrene, *o*-methylstyrene, *p*-*t*-butylstyrene, dimethylstyrene or vinylstyrene.
- 20 14. A copolymer according to any one of the preceding claims, in which said conjugated diene is butadiene, isoprene or piperylene.
- 20 15. A copolymer according to any one of the preceding claims, in which said alkenyl aromatic compound is styrene and said conjugated diene is butadiene.
- 25 16. A process for preparing a block copolymer of an alkenyl aromatic compound and a conjugated diene, said copolymer having a combined alkenyl aromatic compound content of from 25 to 95% by weight and being as claimed in claim 1, which process comprises:
- 25 (a) adding to an organolithium initiator in a hydrocarbon solvent an alkenyl aromatic compound in an amount of from 8 to 45% by weight of the total amount of monomers used in the process, and substantially completely polymerising the same;
- 30 (b) thereafter, adding, in from 2 to 10 portions, a mixture of from 15 to 97% by weight of a conjugated diene and from 3 to 85% by weight of the same alkenyl aromatic compound as in step (a), these percentages being based on the weight of the mixture in step (b), and substantially completely polymerising the mixture after addition of each portion; and
- 35 (c) thereafter, adding the same alkenyl aromatic compound as in step (a) in an amount of from 8 to 45% by weight of the total amount of monomers used in the process and polymerising the same.
- 35 17. A process for preparing an elastomeric block copolymer of an alkenyl aromatic compound and a conjugated diene, said copolymer having a combined alkenyl aromatic compound content of from 25 to 55% by weight and being as claimed in claim 5, which process comprises:
- 40 (a) adding to an organolithium initiator in a hydrocarbon solvent an alkenyl aromatic compound in an amount of from 8 to 40% by weight of the total amount of monomers used in the process, and substantially completely polymerising the same;
- 40 (b) thereafter, adding, in from 2 to 10 portions, a mixture of from 85 to 97% by weight of a conjugated diene and from 3 to 15% by weight of the same alkenyl aromatic compound as in step (a), these percentages being based on the weight of the mixture in step (b), and substantially completely polymerising the mixture after addition of each portion; and
- 45 (c) thereafter, adding the same alkenyl aromatic compound as in step (a) in an amount of from 8 to 40% by weight of the total amount of monomers used in the process and polymerising the same.
- 45 18. A process according to claim 17, in which the amount of alkenyl aromatic compound polymerised in step (a) and/or (c) is from 10 to 25% by weight of the total amount of monomers used.
- 50 19. A process according to claim 17 or claim 18, in which, between steps (b) and (c) a conjugated diene is added and polymerised.
- 55 20. A process for preparing a resinous block copolymer of an alkenyl aromatic compound and a conjugated diene, said copolymer having a combined alkenyl aromatic compound content which is greater than 55% by weight but not more than 95% by weight and being as claimed in claim 7, which process comprises:
- 55 (a) adding to an organolithium initiator in a hydrocarbon solvent an alkenyl aromatic compound in an amount of from 20 to 45% by weight of the total amount of monomers used in the process, and substantially completely polymerising the same;
- 60 (b) thereafter, adding, in from 2 to 10 portions, a mixture of from 15 to 97% by weight of a conjugated diene and from 3 to 85% by weight of the same alkenyl aromatic compound as in step (a), these percentages being based on the weight of the mixture in step (b), and substantially completely polymerising the mixture after addition of each portion; and
- 60 (c) thereafter, adding the same alkenyl aromatic compound as in step (a) in an amount of from 20

- to 45% by weight of the total amount of monomers used in the process and polymerising the same.
21. A process according to claim 20, in which the alkenyl aromatic compound in step (a) and/or (c) is added in an amount of from 25 to 40% by weight of the total amount of monomers used. 5
22. A process according to claim 20 or claim 21, in which, between steps (b) and (c), a conjugated diene is added and polymerised.
23. A process according to any one of claims 16 to 22, in which said hydrocarbon solvent is cyclopentane, cyclohexane, benzene, ethylbenzene or xylene or a mixture of one of these solvents with pentane, hexane, heptane or butane.
- 10 24. A process according to any one of claims 16 to 23, in which said organolithium compound is butyllithium, sec-butyllithium, t-butyllithium, hexyllithium, isohexyllithium, phenyllithium or naphthyllithium. 10
25. A process according to any one of claims 16 to 24, in which said organolithium initiator is employed in an amount of from 0.04 to 1.0 part by weight per 100 parts by weight of monomers.
- 15 26. A process according to any one of claims 16 to 25, in which an ether or a tertiary amine is present with said organolithium compound in said hydrocarbon solvent. 15
27. A process according to claim 26, in which said ether or amine is tetrahydrofuran, diethyl ether, anisole, dimethoxybenzene, ethylene glycol dimethyl ether, triethylamine, N,N-dimethylaniline or pyridine.
- 20 28. A process according to claim 17, substantially as hereinbefore described with reference to any one of the foregoing Examples 1 to 7. 20
29. A process according to claim 20, substantially as hereinbefore described with reference to any one of the foregoing Examples 9 to 12.
30. A copolymer according to claim 1, substantially as hereinbefore described with reference to 25 any one of the foregoing Examples 1 to 7.
31. A copolymer according to claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples 9 to 12.

Printed in the United Kingdom for Her Majesty's Stationery Office, Demand No. 8818935, 10/1984. Contractor's Code No. 6378.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.